B. Interphase Analysis and Control in Fiber-Reinforced Thermoplastic Composites

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Objectives

- Develop the science underlying the formation and effects of transcrystalline regions in carbon-fiber-reinforced thermoplastic matrix composite systems.
- Exploit the understanding developed from the research described above to allow controlled tailoring of the interphase transcrystallinity for specific applications.
- Analyze processing parameters in new thermoplastic matrix composite technologies, specifically the DRIFT (Direct Reinforcement Fabrication Technology, Southern Research Institute) and the P4 [Programmable Powered Preform Process, Department of Energy (DOE)/Oak Ridge National Laboratories (ORNL)] processes.
- Generate composites with tailored interphases for specific applications of laminates produced by the DRIFT and P4 processes in the FreedomCar and other DOE initiatives in lighter weight vehicles.

Approach

- Choose matrix materials relevant to the FreedomCar and DOE automotive lightweight materials initiatives.
- Characterize the chosen matrix materials with respect to mechanical properties and crystallinity.
- Determine the thermodynamic and practical adhesion between the chosen matrix materials and carbon fibers. The carbon fibers will be both sized and unsized.
- Identify and control the presence and size of transcrystalline regions in the matrix material adjacent to the carbon fibers.
- Manufacture laminates using the DRIFT and P4 processes having controlled transcrystalline regions.
- Perform mechanical testing, including tensile testing, impact testing, and indentation testing of the laminates having controlled interphases.

Accomplishments

- Chose matrix materials—polypropylene (PP), poly(phenylene) sulfide (PPS).
- Manufactured axisymmetric microbond test fixture for practical adhesion measurements.
- Created carbon fiber resistivity/temperature calibration curves and heating device.
- Gave presentation at South Dakota EPSCoR (Experimental Program to Stimulate Competitive Research) Conference.
- Began mechanical testing of component materials.

Future Direction

- Conduct thermodynamic and practical adhesion measurements of PP and PPS with carbon fibers having various (including no) sizings.
- Perform indentation testing of initial DRIFT laminates with Dr. Edgar Lara-Curzio of ORNL and with a new nanoindentation machine recently purchased by the South Dakota School of Mines and Technology (SDSM&T).
- Continue mechanical property determination of matrices and fibers. Much of this work will be performed at SDSM&T, but some single-fiber testing work will be performed at ORNL.
- Begin measurement of the extent of transcrystalline regions in test pieces using a new acoustic force atomic force microscope accessory, to be purchased with funds from this grant.
- Perform static and dynamic mechanical testing of DRIFT and P4 laminates.
- Send at least one student and two of the Principle Investigators to ORNL and the University of Alabama-Birmingham to procure samples, perform testing, and better understand the processing techniques used to fabricate samples.

Introduction

During the past decade, considerable effort has been expended to develop a new generation of vehicles that are lighter and more fuel-efficient than today's vehicles. In addition, these vehicles should retain crashworthiness and be of relatively low cost. Targets include reduction in overall weight of approximately 50%, primarily achieved through lighter body and chassis materials. Polymer matrix composites (PMCs) have reached this target with a potential weight savings of 70%. At the current time, PMC technology has, in general, been deemed too costly, because carbon-fiber-based PMCs can cost ten times as much as steel parts. Some of this increased cost is due to the high price of carbon fibers and some due to limitations in the manufacturing process. Many of the problems in the manufacturing process are caused or exacerbated by lack of fundamental scientific knowledge of the interactions between the fibers and matrix materials.

This research is of significance to the Department of Energy (DOE) Automotive Lightweighting Materials Program because it will help develop the necessary science base to allow greater exploitation of PMCs having thermoplastic matrices. Traditionally, these materials have trailed the use of PMCs having thermoset matrices, because of processability issues stemming from the low viscosity and wetting of the thermoplastic matrix material. In addition, thermoplastic matrices are generally less strong and less stiff than thermoset matrices. This liability is further compounded by the fact that most fiber reinforcements associated with thermoplastic matrix PMCs are of fairly short length, mainly because of the processing limitations mentioned earlier. This latter aspect is relevant because short-fiber reinforcements do not carry load as well as long or continuous fiber reinforcements. From the automotive perspective, short-fiber-reinforced PMCs are therefore most utilized in nonstructural components. Further comparisons between thermoplastic and thermoset matrix PMCs

are warranted here to highlight the focus of this research project, namely the role of the interface/ interphase region between the fiber and the matrix.

The development of the interphase in thermoplastic PMCs is quite different from that of thermosetting matrices, which tend to be amorphous in nature. Rather, in thermoplastic PMCs, the interphase development is generally due to nucleation and growth of crystallites from the fiber surface rather than actual chemical reactions within the interphase. The interphases formed in these systems are termed transcrystalline regions, reflecting their dependence upon the thermoplastic crystallinity. There has been much speculation in the literature as to the cause for the formation of the transcrystalline region and its role in bulk composite properties. Several conclusions can be reached. First, the transcrystalline region can grow in size to tens of microns, depending upon such parameters as fiber type, morphology, and fiber surface treatments such as sizings. Second, the transcrystalline region can significantly affect properties such as the strength and impact resistance. Also, in some cases different types of transcrystalline interphases may be formed. For instance, both α and β transcrystalline regions were produced around natural fibers in polypropylene matrix composites. These regions could be altered by inclusion of maleic anhydride in the polypropylene or on the fiber.

With respect to these novel processing routes, two examples are of particular interest to this research. The first is a low-cost process to produce continuous reinforcing fibers with thermoplastic matrices, called the **D**irect **Rei**nforcement **F**abrication **T**echnology (DRIFT) developed by the Southern Research Institute (SRI). PMCs produced by this continuous fiber technology could serve as metal-replacements in structural applications, specifically for the automotive industry. Keys to optimal utilization of the DRIFT process are fiber wetting, and ultimately adhesion, of the thermoplastic matrix. Traditionally, sizings are applied to the fibers to help prevent abrasive damage, and assist with lubrication. A major component of the sizing is a coupling agent that aids in wetting, adhesion, and hygrothermal stability of the composite. Research conducted in this program will utilize thermoplastic matrix PMCs produced by SRI using the DRIFT process. The second novel processing route of interest is the **P**rogrammable **P**owered **P**reform **P**rocess (P4). While the P4 technology does allow control over fiber length, its main potential benefit is its ability to circumvent previous PMC process limitations through robotic control. To our knowledge, no fundamental analysis of PMC interphases formed by the P4 technology has been undertaken.

This research program builds upon a multidisciplinary effort with a vast background in interphase analysis and control in thermosetting PMC systems and applies this wealth of experience to new thermoplastic matrix PMC systems critical to the future success of the Automotive Lightweighting Materials Program. The research will investigate model systems deemed of interest by members of the Automotive Composites Consortium (ACC) as well as samples at the forefront of PMC process development (DRIFT and P4 technologies). Finally, the research will investigate, based upon the fundamental understanding of the interphases created during the fabrication of thermoplastic PMCs, the role the interphase plays in key bulk properties of interest to the automotive industry.

Project Deliverables

This research will provide a better understanding of the science, particularly with respect to adhesion, of thermoplastic matrices with fiber reinforcements. The adhesion data will be used to identify processing parameters for thermoplastic matrix composites to tailor transcrystalline interphase formation. Transcrystalline interphases are generally quite large (>10 μm) and can be stronger and stiffer than the matrix material or tougher and with greater work of fracture than the matrix. In addition, this work will produce composite samples using new processing technologies and the scientific knowledge gained with respect to adhesion and interphase formation. These test protocols are important to possible end uses for the tailored PMCs in automotive applications.

Accomplishments

Research accomplishments during the past year occurred in three primary areas: adhesion, mechanical property determination, and extent of crystallinity as a function of formation conditions. Progress in each of the three areas is described below.

Adhesion

Adhesion research was divided into two areas, thermodynamic adhesion and practical adhesion. Thermodynamic adhesion includes the measurement of the work of adhesion between each polymer and fiber combination through the determination of the drop geometry and hence three-phase contact angle. Practical adhesion is the polymer/fiber adhesion measured through micromechanical testing such as the microbond test or the microindentation test. In thermodynamic adhesion progress, drop shapes for a variety of polymer beads on carbon fibers have been measured and the contact angles found. A typical drop is shown in Figure 1. This work is ongoing. In addition, methods of heating the fiber, as in the DRIFT process, have been developed. Also, techniques for measuring the fiber temperature were derived. Currently, the best method involves resistively heating the fibers through the application of an applied voltage. This process was modeled through a finite-difference, heat-transfer model. The model is used to back calculate the temperature, as the resistance as a function of temperature for the fibers has been measured experimentally.
Figures 2–4 contain graphs of the fiber resistivity curve, the fiber temperature as a function of length, and power vs temperature for a resistively heated fiber. In Figure 2, the resistivity was found to vary with the length of the fiber used, but the slope of the resistivity was relatively constant for all fiber lengths until fiber oxidation began at about 250–300ºC. In Figure 3, the temperature distribution away from the heatsink at a fiber end was found using the equations listed with the figure. Within 2 μm from the heatsink, the fiber has achieved a constant temperature. In Figure 4, a carbon fiber was resistively heated and the temperature predicted from the data in Figure 2. A small polypropylene (PP) chevron was placed on the fiber during heating, and the point of PP melting was found from visual observation. The PP melting point was slightly higher than measured in bulk PP, which could be due to heat transfer effects, differences between the types of fibers used, or the method of observation.

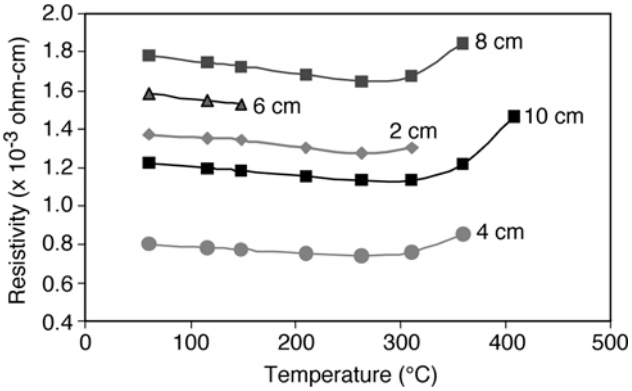
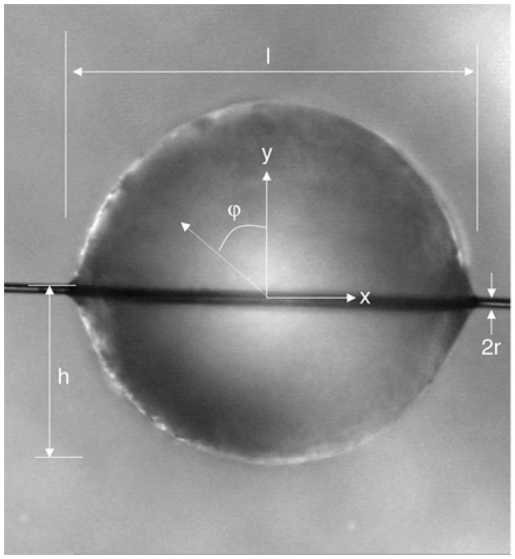


Figure 2. Measured carbon fiber resistivity as a function of applied temperature.



$x = \pm[arF(\varphi, k) + hE(\varphi, k)]$,

$y^2 = h^2(1 - k^2\sin^2\varphi)$,

$a = f$ (contact angle, geometry)
$h = f$ (geometry)
$k = f(a, h)$
F, E are Legendre integrals

$y_{max} = h$
$x_{max} = 1/2$

Figure 1. Polypropylene bead on carbon fiber.

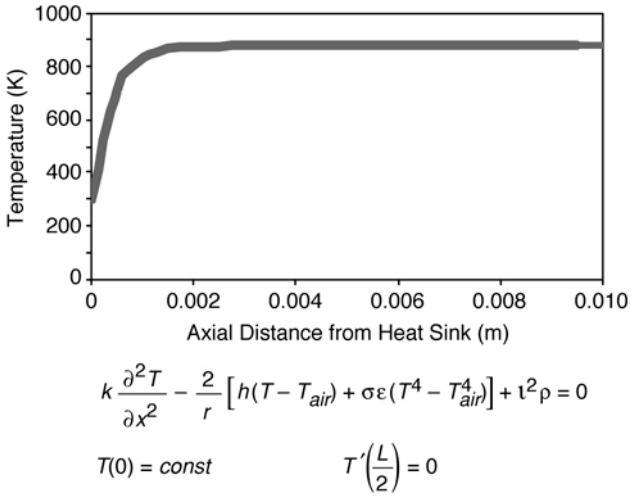


Figure 3. Predicted temperature profile of carbon fiber away from heatsink. Equations at bottom of figure were those used to make the profile prediction.

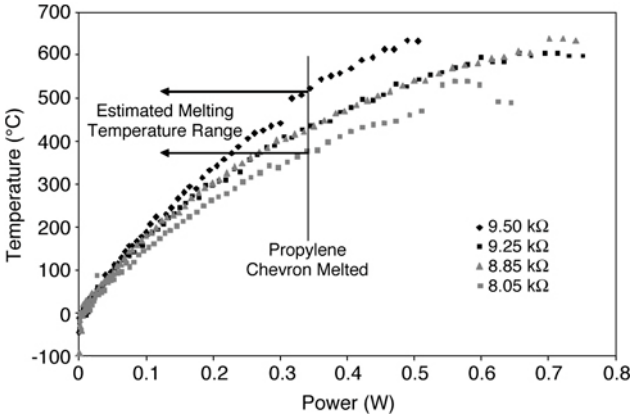


Figure 4. Predicted temperature versus applied voltage for carbon fiber. The data in Figure 2 was used to predict the temperature.

For practical adhesion, a new device for performing the microbond test has been developed to take advantage of the load resolution of our new dynamic mechanical analysis (DMA) equipment. The load resolution of our new system is approximately 2 orders of magnitude better than our previous device. In addition, the new device utilizes a laser-fabricated circular aperture to allow the force to be distributed more evenly on the bead than the previous parallel vise setup. Consequently, the new device yields a less complex stress distribution that is also more readily modeled using finite-element analysis, resulting in more meaningful test results. This new device is currently being evaluated with a variety of systems including PP/carbon fiber that had been manufactured for thermodynamic adhesion measurements.

Mechanical Property Determination

The mechanical properties of the component materials were examined during year 1. With respect to the matrix materials, DMA of the PP has been conducted. This was used to determine the storage and loss modulus of the materials as a function of temperature. Tensile testing of the PP material has been initiated. Thus far, these experiments have been conducted as a function of strain rate for PPs having little crystallinity. With this strain rate knowledge, tensile testing using biaxial or rosette strain gages is being conducted to simultaneously determine the Young's modulus, yield strength, postyield behavior, and the Poisson's ratio. For fiber testing, a new device for testing single fibers has been made. This device is similar to that mentioned in the adhesion discussion because it uses the DMA to achieve good force resolution. As this device is undergoing final testing to ensure its proper functioning, fiber tensile testing is set to begin within the next few weeks.

Extent of Crystallinity as a Function of Formation Conditions

The research conducted in this area over the past year has been primarily aimed at determining conditions by which transcrystalline regions are formed in the PP-carbon fiber systems. The initial work in this area was to perform differential scanning calorimetry (DSC) to determine the extent of crystallinity of the initial material and the effect of cooling rate on crystallite formation. Figure 5 shows a standard DSC curve for the PP used herein. In Figure 5, the degree of crystallization is relatively constant for three different cooling rates, probably due to using the same time at the melting temperature for all samples. This research is ongoing as additional parameters such as time in the melted state and temperature difference between the maximum test temperature and the melting point are important to crystallite formation. In addition, the best methods for obtaining surfaces suitable for atomic force microscopy, both acoustic and phase

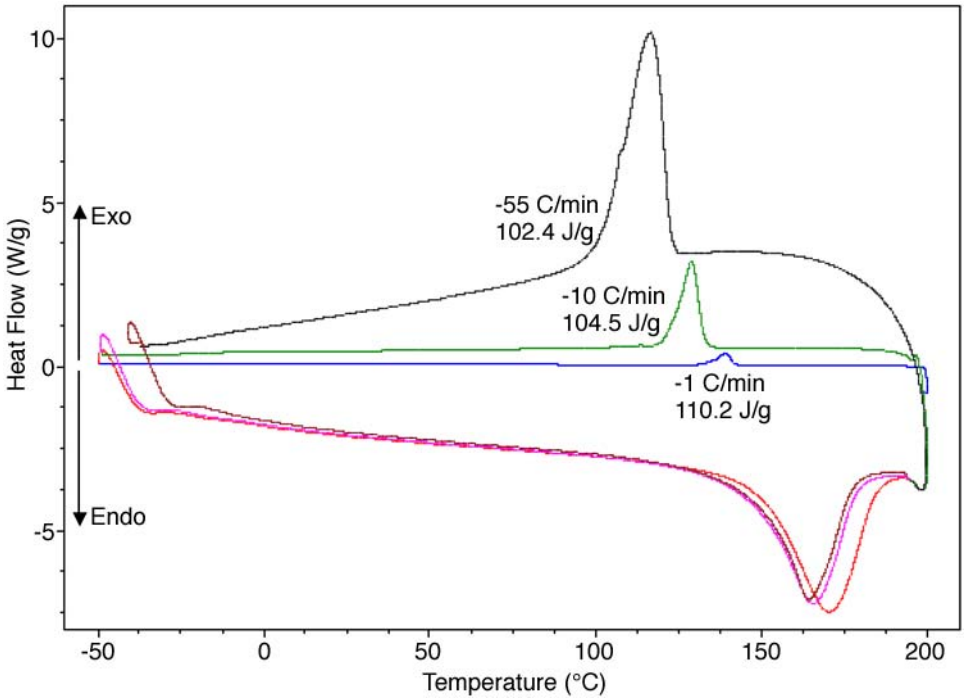


Figure 5. Differential scanning calorimetry curves for polypropylene at various cooling rates.

imaging, are currently under investigation. In particular, the behavior of carbon fibers during microtoming may result in damage to the near-fiber region, inhibiting the finding and interrogation of transcrystalline regions. Therefore, this may necessitate a change in AFM sample preparation.

Summary

Highlights of our FY 2004 research include:

1. Chose matrix materials—PP and PPS.
2. Manufactured axisymmetric microbond test fixture for practical adhesion measurements.
3. Created carbon fiber resistivity/temperature calibration curves and heating device.
4. Presented initial work at South Dakota EPSCoR Conference.
5. Began mechanical testing of component materials.

Presentation

1. T. Engstrom, S. Bickett, J. Ash, W. Cross, L. Kjerengtroen, J. Kellar, and R. Norris, "Interphase Analysis and Control in Fiber Reinforced Thermoplastic Composites," presented at the South Dakota EPSCoR Annual Meeting, September 2004.